Kinetic modelling of radiochemical ageing of ethylene–propylene copolymers

Xavier Colin [a,*], Emmanuel Richaud [a,b], Jacques Verdu [a], Carole Monchy-Leroy [b]

[a] LIM, Arts et Métiers ParisTech, 151 boulevard de l'Hôpital, 75013 Paris, France
[b] EDF R&D, Avenue des Renardières, Ecuelles, 77818 Moret-sur-Loing, France

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A non-empirical kinetic model has been built for describing the general trends of radiooxidation kinetics of ethylene–propylene copolymers (EPR) at low γ dose rate and low temperature. It is derived from a radical chain oxidation mechanism composed of 30 elementary reactions: 19 relative to oxidation of methylene and methyne units plus 11 relative to their eventual cooxidation. The validity of this model has been already checked successfully elsewhere for one homopolymer: polyethylene (PE) (Khelidj et al., 2006a,b; Colin et al., 2007). In the present study, it is now checked for polypropylene (PP) and a series of three EPR differing essentially by their mole fraction of ethylene (37%, 73% and 86%) and their crystallinity degree (0%, 5% and 26%). Predicted values of radiation-chemical yields are in good agreement with experimental ones published in the last half past century.

1. Introduction

Radiooxidation of saturated hydrocarbons polymers (PE, PP and their EPR copolymers) at low γ dose rate at low temperature has been intensively studied in the past half century (e.g. Decker et al., 1973; Carlsson, 1993). It is now well demonstrated that there is a complex radical chain reaction initiated both by the polymer radiolysis and the thermolysis of its main propagation product: the hydroperoxide group (Colin et al., 2007). For a long time, such a mechanism was considered out of reach of any kinetic modelling. Indeed, the resulting "stiff" system of differential equations (SSDE) could not be solved without the use of a series of simplifying assumptions, which could lead to serious inaccuracies and thus, a distortion of the physical sense of mechanism. These assumptions are:

1. Unicity of reactive site. All the reactive products involved in this mechanism are derived from only one reactive site corresponding to the carbon bonded to the most abstractable hydrogen atom. As an example, one can quote methynic carbon in PP;
2. Existence of a steady-state regime. The reaction reaches rapidly an equilibrium in which the hydroperoxides and radicals concentrations are constant;
3. Long kinetic chain. This assumption can be applied when oxidation is essentially initiated by the polymer radiolysis. In this case, one applies an additional assumption;
4. Stability of hydroperoxide groups. This assumption is valid, of course, below a certain ceiling in the time–temperature map;
5. Oxygen excess. All alkyl radicals are considered almost instantaneously transformed into peroxyl ones and thus, only one termination reaction, involving these latter, can be taken into account. On the contrary, when oxygen is not in excess, two additional terminations involving alkyl radicals have to be considered, which leads authors to propose an additional assumption:
6. Existence of an interrelationship between the termination rate constants. This is an ad hoc assumption, aimed to simplify the calculations considerably.
7. Microheterogeneity linked to low radical mobility. If diffusion control operates on an elementary reaction, it is first on termination because it involves the reactive species in the lowest concentration. Ideally a diffusion law might be introduced in the expression of kinetic rate constants. This is currently under investigation in our laboratory but (for the moment), we will use an artefact consisting to consider radicals escape from the cage as a simple chemical equation characterized by its first order rate constant. This is, no doubt, an oversimplification. However, it can be considered as a first approach of the role of the molecular mobility on the efficiency of termination.

Kinetics are assumed to be monochronal rather than polychronal (Emanuel and Buchachenko, 1987) because we are unable at this state of our knowledge to distinguish between which both types of processes and a fortiori, to identify the parameters of polychronality in the frame of this type of study. In other words,

* Corresponding author. Fax: +33 1 44 24 62 90.
E-mail address: xavier.colin@paris.ensam.fr (X. Colin).

for each elementary rate constant, we will consider a single (average) value equivalent to the real distribution. We believe that, in rubbers or semi-crystalline polymers having their amorphous phase in rubbery state, oxidation is homogeneous (in the amorphous phase). Our arguments have been reported elsewhere (Fayolle et al., 2008). In semi-crystalline polymers, the local (in amorphous phase) concentration C_a of reactive species is linked to the global (measured) concentration C_g by:

$$C_g = C_a(1 - x_C)$$

x_C being the degree of crystallinity.

In the last decade, the use of efficient commercially available numerical tools (Hairer and Wanner, 1991), dedicated to the resolution of stiff problems of chemical kinetics, has allowed us to eradicate practically all these simplifying assumptions, except assumption 1 (Colin et al., 2004). Since the number of elementary reactions increases quasi-exponentially with the number of distinct reactive sites, we were face to the following problem: How to solve the "inverse problem"? I.e. to determine the numerous rate constants from experimental results?

In the case of EPR copolymers containing two distinct reactive sites (methylenic and methynic carbons), the problem simplifies considerably because many rate constants have been already determined previously for PE (Khelidj et al., 2006a,b; Colin et al., 2007). The remaining rate constants can be now reasonably determined on PP (in this case, PP will be considered as an alternate copolymer of methylene and methyne units) and/or a series of EPR differing by their mole fraction of ethylene. The literature on cooxidation kinetics has been recently reviewed by Denisov and Afanas'ev (2005). Papers on cooxidation of hydrocarbon polymers are very scarce in the last 20 years. Kinetic models elaborated in the 1960s are based on the hypotheses 1, 2, 3, 4, 5, 6 and 7. Decker et al. (1973) considered (from the kinetic point of view) ethylene–propylene copolymers as virtual homopolymers characterized by a single rate constant value. It seemed to us possible to make one step beyond starting from more realistic hypotheses. The present study does not pretend to give the definitive solution to this difficult problem but rather to test the feasibility of our approach.

2. Kinetic model

In a first approximation, the mechanism of PP and EPR radiooxidation at low γ dose rate and low temperature can be written as follows:

1i) $(1-\gamma)P_TH+\gamma P_SH+h\nu \rightarrow (1-\gamma)P_T^o+\gamma P_S^o+1/2H_2$ (r_i)

1bT) $2P_TOOH \rightarrow (1-\gamma)P_T^o+\gamma P_S^o+P_TO_2^o+\gamma_{1T}P_T=O$ (k_{1bT})

1bS) $2P_SOOH \rightarrow \gamma P_S^o+(1-\gamma)P_T^o+P_SO_2^o+\gamma_{1S}P_S=O$ (k_{1bS})

1bTS) $P_TOOH+P_SOOH \rightarrow (1-\gamma)P_T^o+\gamma P_S^o+P_SO_2^o+\gamma_{1T}P_T=O$ (k_{1bTS})

1bST) $P_SOOH+P_TOOH \rightarrow \gamma P_S^o+(1-\gamma)P_T^o+P_TO_2^o+\gamma_{1S}P_S=O$ (k_{1bST})

rT) $P_T^o \rightarrow P_S^o+F$ (k_{rT})

2T) $P_T^o+O_2 \rightarrow P_TO_2^o$ (k_{2T})

2S) $P_S^o+O_2 \rightarrow P_SO_2^o$ (k_{2S})

3T) $P_TO_2^o+P_TH \rightarrow P_TOOH+P_T^o$ (k_{3T})

3S) $P_SO_2^o+P_SH \rightarrow P_SOOH+P_S^o$ (k_{3S})

3TS) $P_TO_2^o+P_SH \rightarrow P_TOOH+P_S^o$ (k_{3TS})

3ST) $P_SO_2^o+P_TH \rightarrow P_SOOH+P_T^o$ (k_{3ST})

4T) $P_T^o+P_T^o \rightarrow$ inactive products (k_{4T})

4S) $P_S^o+P_S^o \rightarrow$ inactive products (k_{4S})

4TS) $P_T^o+P_S^o \rightarrow$ inactive products (k_{4TS})

5T) $P_T^o+P_TO_2^o \rightarrow (1-\gamma_{5T})P_TOOH$+inactive products (k_{5T})

5S) $P_S^o+P_SO_2^o \rightarrow (1-\gamma_{5S})P_SOOH$+inactive products (k_{5S})

5TS) $P_T^o+P_SO_2^o \rightarrow (1-\gamma_{5TS})P_SOOH$+inactive products (k_{5TS})

5ST) $P_S^o+P_TO_2^o \rightarrow (1-\gamma_{5ST})P_TOOH$+inactive products (k_{5ST})

60T) $P_TO_2^o+P_TO_2^o \rightarrow [P_TO^o\ {}^oOP_T]_{cage}+O_2$ (k_{60T})

61T) $[P_TO^o\ {}^oOP_T]_{cage} \rightarrow P_TO{-}OP_T$ (k_{61T})

63T) $[P_TO^o\ {}^oOP_T]_{cage} \rightarrow 2(1-\gamma)P_T^o+2\gamma P_S^o+2\gamma_{1T}P_T=O$ (k_{63T})

60S) $P_SO_2^o+P_SO_2^o \rightarrow [P_SO^o\ {}^oOP_S]_{cage}+O_2$ (k_{60S})

61S) $[P_SO^o\ {}^oOP_S]_{cage} \rightarrow P_SO{-}OP_S$ (k_{61S})

62S) $[P_SO^o\ {}^oOP_S]_{cage} \rightarrow P_S{-}OH+P_S=O$ (k_{62S})

63S) $[P_SO^o\ {}^oOP_S]_{cage} \rightarrow 2\gamma P_S^o+2(1-\gamma)P_T^o+2\gamma_{1S}P_S=O$ (k_{63S})

60TS) $P_TO_2^o+P_SO_2^o \rightarrow [P_TO^o\ {}^oOP_S]_{cage}+O_2$ (k_{60TS})

61TS) $[P_TO^o\ {}^oOP_S]_{cage} \rightarrow P_TO{-}OP_S$ (k_{61TS})

62TS) $[P_TO^o\ {}^oOP_S]_{cage} \rightarrow P_T{-}OH+P_S=O$ (k_{62TS})

63TS) $[P_TO^o\ {}^oOP_S]_{cage} \rightarrow 2(1-\gamma)P_T^o+2\gamma P_S^o+\gamma_{1S}P_S=O+\gamma_{1T}P_T=O$ (k_{63TS})

where P_S and P_T represent methylenic and methynic carbons respectively, and F a double bond; γ is a partition coefficient: $\gamma = [P_sH]/[P_TH]+[P_SH]$, ranging between 0.5 (since $[P_sH] = [P_TH]$ for PP) and 1 ($[P_TH] = 0$ for PE); and r_i the global initiation rate: $r_i \approx 10^{-7}(\gamma G_{iS}+(1-\gamma)G_{iT})\ \bar{D}$, G_{iS} and G_{iT} being the respective radiation radical yields for PE (i.e. $G_iP_E = G_{iS}$) and a virtual homopolymer composed only of methyne units, both expressed in number of radicals per 100 eV of absorbed energy. Thus, for PP, one can write: $G_{iPP} = 0.5\ G_{iS}+0.5\ G_{iT}$. γ_{1T} and γ_{1S} are the respective yields of carbonyl groups formation in the corresponding elementary reactions.

Reaction (rT) is a rearrangement of tertiary alkyl radical P_T^o (by β chain scission), currently used by practitioners to elaborate low molar mass PP at high temperature (Mita, 1978), but of which the existence in the case of γ irradiation at low temperature remains to be demonstrated yet.

Classically, hydrogen abstraction by alkyl radicals is ignored in the kinetic analysis because it does not have a direct influence on kinetics. As mentioned by a referee, the situation is different here because these reactions can modify the distribution of P_S^o and P_T^o sites. Provisionally, it will be assumed that the influence of these reactions is negligible compared to the one of the various cross reactions and radicals rearrangement taken into account. No doubt, these reactions have to be introduced in the future versions of this model.

The writing of reactions (1b) was given with more details by Audouin et al. (1995). Here, macro-alcohols P_S–OH and P_T–OH are generated (with complementary yield of the one for carbonyl) by 1bT, 1bS, 1bST and 1bTS reactions (and also in 63S, 63T and 63TS ones), but since these species are not used for model validation, they are not mentioned for the sake of clarity.

Dialkylperoxides are formed from P^o+POO^o reactions. They are denoted as inactive products because their decomposition is considerably slower than POOH one and is therefore neglected here.

This mechanism leads to the following SSDE:

$$\frac{d[P_T^o]}{dt} = (1-\gamma)r_i + (1-\gamma)k_{1bT}[P_TOOH]^2 + (1-\gamma)k_{1bTS}[P_TOOH][P_SOOH] + (1-\gamma)k_{1bST}[P_SOOH][P_TOOH] - k_{rT}[P_T^o] - k_{2T}[P_T^o][O_2] + k_{3T}[P_TO_2^o][P_TH] + k_{3ST}[P_SO_2^o][P_TH] - 2k_{4T}[P_T^o]^2 - k_{4TS}[P_T^o][P_S^o] - k_{5T}[P_T^o][P_TO_2^o] - k_{5TS}[P_T^o][P_SO_2^o] + 2(1-\gamma)k_{63T}[P_TO^o\,{}^oOP_T]_{cage} + 2(1-\gamma)k_{63S}[P_SO^o\,{}^oOP_S]_{cage} + 2(1-\gamma)k_{63TS}[P_TO^o\,{}^oOP_S]_{cage}$$

$$\frac{d[P_S^o]}{dt} = \gamma r_i + \gamma k_{1bT}[P_TOOH]^2 + \gamma k_{1bTS}[P_TOOH][P_SOOH] + \gamma k_{1bST}[P_SOOH][P_TOOH] + k_{rT}[P_T^o] - k_{2S}[P_S^o][O_2] + k_{3S}[P_SO_2^o][P_SH] + k_{3TS}[P_TO_2^o][P_SH] - 2k_{4S}[P_S^o]^2 - k_{4TS}[P_T^o][P_S^o] - k_{5S}[P_S^o][P_SO_2^o] - k_{5ST}[P_S^o][P_TO_2^o] + 2\gamma k_{63T}[P_TO^o\,{}^oOP_T]_{cage} + 2\gamma k_{63S}[P_SO^o\,{}^oOP_S]_{cage} + 2\gamma k_{63TS}[P_TO^o\,{}^oOP_S]_{cage}$$

$$\frac{d[P_TO_2^o]}{dt} = k_{1bT}[P_TOOH]^2 + k_{1bST}[P_SOOH][P_TOOH] + k_{2T}[P_T^o][O_2] - k_{3T}[P_TO_2^o][P_TH] - k_{3TS}[P_TO_2^o][P_SH] - k_{5T}[P_T^o][P_TO_2^o] - k_{5ST}[P_S^o][P_TO_2^o] - 2k_{60T}[P_TO_2^o]^2 - k_{60TS}[P_TO_2^o][P_SO_2^o]$$

$$\frac{d[P_SO_2^o]}{dt} = k_{1bS}[P_SOOH]^2 + k_{1bTS}[P_TOOH][P_SOOH] + k_{2S}[P_S^o][O_2] - k_{3S}[P_SO_2^o][P_SH] - k_{3ST}[P_SO_2^o][P_TH] - k_{5S}[P_S^o][P_SO_2^o] - k_{5TS}[P_T^o][P_SO_2^o] - 2k_{60S}[P_SO_2^o]^2 - k_{60TS}[P_TO_2^o][P_SO_2^o]$$

$$\frac{d[P_TOOH]}{dt} = -2k_{1bT}[P_TOOH]^2 - k_{1bTS}[P_TOOH][P_SOOH] - k_{1bST}[P_SOOH][P_TOOH] + k_{3T}[P_TO_2^o][P_TH] + k_{3TS}[P_TO_2^o][P_SH] + (1-\gamma_{5T})k_{5T}[P_T^o][P_TO_2^o] + (1-\gamma_{5ST})k_{5ST}[P_S^o][P_TO_2^o]$$

$$\frac{d[P_SOOH]}{dt} = -2k_{1bS}[P_SOOH]^2 - k_{1bTS}[P_TOOH][P_SOOH] - k_{1bST}[P_SOOH][P_TOOH] + k_{3S}[P_SO_2^o][P_TH] + k_{3ST}[P_SO_2^o][P_TH] + (1-\gamma_{5S})k_{5S}[P_S^o][P_SO_2^o] + (1-\gamma_{5TS})k_{5TS}[P_T^o][P_SO_2^o]$$

$$\frac{d[P_TO^o\,{}^oOP_T]_{cage}}{dt} = k_{60T}[P_TO_2^o]^2 - (k_{61T}+k_{63T})[P_TO^o\,{}^oOP_T]_{cage}$$

$$\frac{d[P_SO^o\,{}^oOP_S]_{cage}}{dt} = k_{60S}[P_SO_2^o]^2 - (k_{61S}+k_{62S}+k_{63S})[P_SO^o\,{}^oOP_S]_{cage}$$

$$\frac{d[P_TO^o\,{}^oOP_S]_{cage}}{dt} = k_{60TS}[P_TO_2^o][P_SO_2^o] - (k_{61TS}+k_{62TS}+k_{63TS})[P_TO^o\,{}^oOP_S]_{cage}$$

with $[O_2] = S \times p_{O_2}$ (Henry's law), S being the coefficient of oxygen solubility into the polymer and p_{O_2} the oxygen partial pressure in the surrounding atmosphere.

Since the substrate consumption is not taken into account here, this model is valid only for relatively low conversions but we know that important use properties, especially fracture ones, decrease catastrophically at low conversions (Fayolle et al., 2008).

This system can be solved numerically using the ODE23s Solver (of Matlab) with the following initial conditions (when $t = 0$):

$$[P_T^o] = [P_S^o] = 0; [P_TO_2^o] = [P_SO_2^o] = 0; [P_TO^o\,{}^oOP_T]_{cage} = [P_SO^o\,{}^oOP_S]_{cage} = [P_TO^o\,{}^oOP_S]_{cage} = 0; \text{ and } \frac{1}{1-\gamma}[P_TOOH] = \frac{1}{\gamma}[P_SOOH] = 10^{-3} - 10^{-2}\,mol\,l^{-1}.$$

It gives access to the changes (against time) of the overall concentration of reactive products:

Alkyl: $[P^o] = [P_T^o]+[P_S^o]$, and peroxyl radicals: $[PO_2^o] = [P_TO_2^o]+[P_SO_2^o]$;

Hydroperoxides: $[POOH] = [P_TOOH]+[P_SOOH]$;

And cage paired alkoxyl radicals:

$$Q = [P_TO^o\,{}^oOP_T]_{cage} + [P_SO^o\,{}^oOP_S]_{cage} + [P_TO^o\,{}^oOP_S]_{cage}.$$

However, only a few of these quantities are accessible experimentally: [POOH] can be determined by iodometric titration and, in most favourable cases, $[P^o]$ and $[PO_2^o]$ by ESR spectroscopy. To check the validity of the previous mechanism, it is thus necessary to calculate many other quantities measurable by conventional laboratory techniques (such as gas analysis, FTIR or NMR spectroscopy, rheometry, etc…).

As an example, molecular hydrogen comes from polymer radiolysis, and oxygen is consumed in propagation and re-emitted in the bimolecular combination of peroxyl radicals, so that:

$$\frac{d[H_2]}{dt} = \frac{1}{2}r_i$$

$$\frac{d[O_2]}{dt} = k_{2S}[P_S^o][O_2] + k_{2T}[P_T^o][O_2] - k_{60T}[P_TO_2^o]^2 - k_{60S}[P_SO_2^o]^2 - k_{60TS}[P_TO_2^o][P_SO_2^o]$$

Double bonds come from the rapid rearrangement (by β scission) of P_T^o radicals and are formed in terminations (by disproportionation of radicals):

$$\frac{d[F]}{dt} = k_{rT}[P_T^o] + (1-\gamma_{4T})k_{4T}[P_T^o]^2 + (1-\gamma_{4S})k_{4S}[P_S^o]^2 + (1-\gamma_{4TS})k_{4TS}[P_T^o][P_S^o] + (1-\gamma_{5T})k_{5T}[P_T^o][P_TO_2^o] + (1-\gamma_{5S})k_{5S}[P_S^o][P_SO_2^o] + (1-\gamma_{5T})k_{5T}[P_T^o][P_TO_2^o] \times + (1-\gamma_{5S})k_{5S}[P_S^o][P_SO_2^o] + (1-\gamma_{5TS})k_{5TS}[P_T^o][P_SO_2^o] + (1-\gamma_{5ST})k_{5ST}[P_S^o][P_TO_2^o]$$

Carbonyl groups come from the rapid rearrangement (by β scission) of P_TO^o and P_SO^o radicals and are formed in terminations (by disproportionation of radicals):

$$[P=O] = [P_T=O] + [P_S=O]$$

$$\frac{d[P=O]}{dt} = \gamma_{1T}k_{1bT}[P_TOOH]^2 + \gamma_{1S}k_{1bS}[P_SOOH]^2 + \gamma_{1T}k_{1bTS}[P_TOOH][P_SOOH] + \gamma_{1S}k_{1bST}[P_TOOH][P_SOOH] + k_{62S}[P_SO^o\,{}^oOP_S]_{cage} + k_{62TS}[P_TO^o\,{}^oOP_S]_{cage} + 2\gamma_{1T}k_{63T}[P_TO^o\,{}^oOP_T]_{cage} + 2\gamma_{1S}k_{63S}[P_SO^o\,{}^oOP_S]_{cage} + (\gamma_{1T}+\gamma_{1S})k_{63TS}[P_TO^o\,{}^oOP_S]_{cage}$$

Peroxide bridges are formed in terminations (by coupling of alkoxyl radicals):

$$[POOP] = [P_TOOP_T] + [P_SOOP_S] + [P_TOOP_S]$$

$$\frac{d[POOP]}{dt} = \gamma_{5T}k_{5T}[P_T^o][P_TO_2^o] + \gamma_{5S}k_{5S}[P_S^o][P_SO_2^o] + \gamma_{5TS}k_{5TS}[P_T^o][P_SO_2^o] + \gamma_{5ST}k_{5ST}[P_S^o][P_TO_2^o] + k_{61T}[P_TO^o\ {}^oOP_T]_{cage} + k_{61S}[P_SO^o\ {}^oOP_S]_{cage} + k_{61TS}[P_TO^o\ {}^oOP_S]_{cage}$$

Chain scissions come from the rapid rearrangement of P_T^o, P_TO^o and P_SO^o radicals:

$$\frac{d[CS]}{dt} = k_{rT}[P_T^o] + \frac{d[P=O]}{dt}$$

Crosslinks are formed in terminations (by coupling of radicals):

$$\frac{d[CR]}{dt} = \gamma_{4T}k_{4T}[P_T^o]^2 + \gamma_{4S}k_{4S}[P_S^o]^2 + \gamma_{4TS}k_{4TS}[P_T^o][P_S^o] + \frac{d[POOP]}{dt}$$

At least, radiation-chemical yields for all these reactive and inactive products, expressed in number of products per 100 eV of absorbed energy, are given by:

$$G_Y = \frac{1}{10^{-7}\bar{D}}\frac{d[Y]}{dt}$$

with Y = P^o, PO_2^o, POOH, H_2, O_2, F, P = O, POOP, CS, CR …

3. Results

The model has been tested on experimental results of Decker et al. (1973) obtained on 50 μm thick films for which thickness oxidation gradients were minimized. According to the authors, oxidation occurred in oxygen excess regime in which hydrogen abstraction by P^o and H^o radicals must be negligible.

The previous model contains 40 kinetic parameters: 29 rate constants plus 11 yields. It is impossible to determine all these parameters in one single inverse approach. However, one can envisage determining them progressively from experimental results obtained, first, in case of relatively simple radiochemical ageing, for instance PE and PP homopolymers radiolysis, then in case of more and more complex ones, such as PE and PP radiooxidation, first in when oxygen excess, then oxygen is not in excess. Groups of kinetic parameters, which could be determined according to this method, are reported in Table 1.

However, for some radiochemical ageing (e.g. for cases III and V), the number of unknown parameters is too high yet. Fortunately, propagation rate constants: k_{2T}, k_{2S}, k_{3T}, k_{3S}, k_{3TS} and k_{3ST}, can be determined from well-known structure–property relationships established for model compounds. It is well known that addition of oxygen to P^o radicals (2T, 2S) is very fast. The corresponding rate constant is thus very high and, in first approximation, chemical structure and temperature independent (Kamiya and Niki, 1978):

$$k_{2T} = k_{2S} = 10^8 - 10^9\ l\,mol^{-1}\,s^{-1}$$

On the contrary, the rate constant of hydrogen abstraction by PO_2^o radicals (3T, 3S, 3TS, 3ST) depends on the dissociation energy E_D of the C–H bond involved. Korcek et al. have proposed the following relationships (Korcek et al., 1972):

$k_{3T} = 3.0 \times 10^8 \exp(-65500/RT)$;
$k_{3S} = 1.5 \times 10^{10} \exp(-73000/RT)$;
$k_{3TS} = 1.5 \times 10^9 \exp(-73000/RT)$; and
$k_{3TS} = 3.0 \times 10^9 \exp(-65500/RT)$.

In a first approach, one can also assume the following simplifications:

$k_{1bTS} = k_{1bST} = (k_{1bT} \times k_{1bS})^{1/2}$; $k_{5TS} = k_{5ST}$; and $\gamma_{5TS} = \gamma_{5ST}$.

Table 1
Radiochemical ageings, corresponding mechanism, and kinetic parameters remaining to determine from experimental results (see text).

Radiochemical ageing	Mechanism	Kinetic parameters
(I) PE radiolysis	Reactions (1i, 4S) with $\gamma = 1$	G_{iS}, k_{4S}, γ_{4S}
(II) PP radiolysis	Reactions (1i, rT, 4T, 4TS) with $\gamma = 0.5$	G_{iT}, k_{rT}, k_{4T}, k_{4TS}, γ_{4T}, γ_{4TS}
(III) PE radiooxidation when oxygen is excess	Reactions (1i, 1bS, 2S, 3S, 60S, 61S, 62S, 63S) with $\gamma = 1$	k_{1bS}, k_{2S}, k_{3S}, k_{60S}, k_{61S}, k_{62S}, k_{63S}, γ_{1S}
(IV) PE radiooxidation when oxygen is not in excess	Reactions (1i, 1bS, 2S, 3S, 4S, 5S, 60S, 61S, 62S, 63S) with $\gamma = 1$	k_{5S}, γ_{5S}
(V) PP radiooxidation when oxygen is not in excess	All reactions with $\gamma = 0.5$	k_{1bT}, k_{1bTS}, k_{1bST}, k_{2T}, k_{3T}, k_{3TS}, k_{3ST}, k_{5T}, k_{5TS}, k_{5ST}, k_{60T}, k_{61T}, k_{63T}, k_{60TS}, k_{61TS}, k_{62TS}, k_{63TS}, γ_{1T}, γ_{5T}, γ_{5TS}, γ_{5ST}

Table 2
Radiation-chemical yields for PE and PP in inert atmosphere.

Polymer	$G_{iPE\ or\ PP}$	G_{H_2}	G_F	G_{CR}	G_{CS}
PE	8	4 [4.0–4.1]	2 [1.8]	2 [1.9–2]	–
PP	5.1	2.55 [2.3–2.8]	2.6	0.4 [0.3–0.5]	0.45 [0.3–0.6]

Comparison between calculated values and experimental ones (in brackets) from a literature compilation covering the past half century (e.g. Charlesby, 1960; Chapiro, 1962; Carlsson, 1993).

Table 3
Radiation-chemical yields for thin ldPE, hdPE, IPP and APP films (25 μm thick) exposed at 390 and 1050 Gy h^{-1} at 45 °C under 8.6×10^4 Pa of pure oxygen.

Polymer	$\bar{D}$ (Gy h^{-1})	G_{O_2}	G_{POOH}	G_{POH}	G_{POOP}	G_{PO}
ldPE	390	15.9 [16]	9.2 [9.2]	12.3	3 [3]	4.2 [4.2]
	1050	12 [11.9]	5.5 [5.5]	8	3.1 [3.2]	4.1 [4.1]
hdPE	390	11.9 [12]	5.6 [5.6]	9	3 [3]	3.2 [3.2]
	1050	9.6 [9.7]	3.5 [3.5]	6.2	3 [3]	3.6 [3.6]
IPP	390	132 [132]	107 [111]	120 [123]	5 [3]	15.4 [15.3]
	1050	85 [85]	68 [68]	75 [77]	3.5 [3.0]	11.6 [11.6]
APP	390	156 [156]	131 [119]	144 [140]	4 [4]	12.8 [12.8]
	1050	101 [101]	79 [70]	91 [90]	3.5 [3.5]	9.5 [9.5]

Comparison between calculated values and experimental ones (in brackets) reported by Decker et al. (1973).

The 30 remaining kinetic parameters: 20 rate constants plus 10 yields, have determined from experimental radiation-chemical yields for standard PE and PP radiolysis at low temperature, and ldPE, hdPE, IPP and APP radiooxidation at 390 and 1050 Gy h^{-1} at 45 °C under 8.6×10^4 Pa of pure oxygen. The calculated values are compared to experimental ones reported in the literature in Tables 2 and 3. In both cases it is found a satisfying agreement between the theory and experiments.

The values of the radical yields chosen for standard PE and PP can be found relatively high comparatively to experimental values determined by electron spin resonance (ESR) after γ irradiation at low temperature (77 K). As an example, Dole and co. reported

Table 4
Parameters values used for kinetic modelling.

Parameter	G_{1T}	G_{1S}	k_{1bT}	k_{1bS}	k_{1bTS}	k_{rT}	k_{2T}	k_{2S}	k_{3T}		
Value	2.2	8	5.2×10^{-6}	1.6×10^{-8}	2.9×10^{-7}	5.4	10^{8}	10^{8}	5.3×10^{-3}		
Parameter	k_{3S}	k_{3TS}	k_{3ST}	k_{4T}	k_{4S}	k_{4TS}	k_{5T}	k_{5S}			
Value	1.6×10^{-2}	1.6×10^{-3}	5.3×10^{-2}	10^{10}	8×10^{11}	2.3×10^{11}	10^{7}	10^{11}			
Parameter	k_{5TS}	k_{60T}	k_{61T}	k_{63T}	k_{60S}	k_{61S}	k_{62S}	k_{63S}	k_{60TS}		
Value	2×10^{10}	10	0	10	4.8×10^{6}	4.5×10^{6}	6.3×10^{5}	5.8×10^{6}	10^{3}		
Parameter	k_{61TS}	k_{62TS}	k_{63TS}	γ'_{1T}	γ'_{1S}	γ'_{4T}	γ'_{4S}	γ'_{4TS}	γ'_{5T}	γ'_{5S}	γ'_{5TS}
Value	0	0	10^{3}	0.48	0.57	0	0.5	0	0	0.5	0.06

All rate constants are expressed in $l\,mol^{-1}\,s^{-1}$, except for k_n, k_{60}, k_{61}, k_{62} and k_{63} given in s^{-1}.

Table 5
Examples of radiation-chemical yields predicted for thin ldPE, hdPE, IPP and APP films (25 μm thick) exposed at 390 and 1050 Gy h^{-1} at 45 °C under 8.6×10^{4} Pa of pure oxygen.

Polymer	$\dot{D}$ (Gy h^{-1})	G_{CS}	G_{CR}/G_{CS}
ldPE	390	3.8	0.78
	1050	3.9	0.78
hdPE	390	2.8	1.09
	1050	3.3	0.9
IPP	390	14.8	0.34
	1050	11.3	0.31
APP	390	12.4	0.32
	1050	9.3	0.38

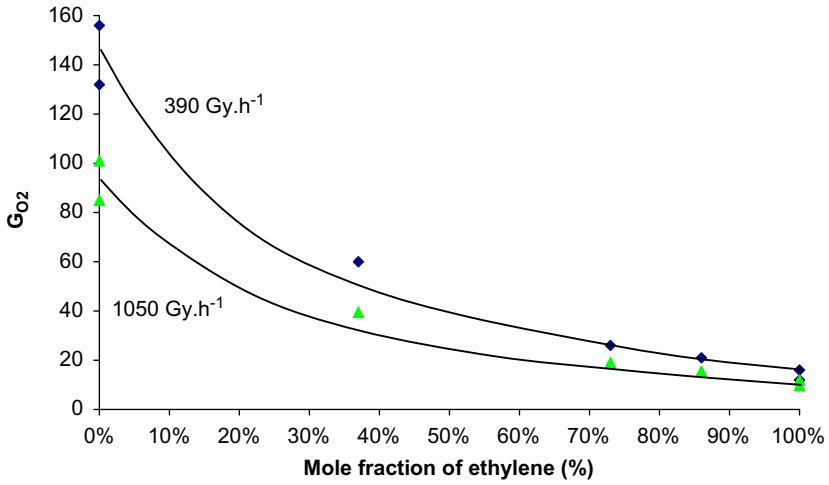

Fig. 1. Radiation-chemical yield for oxygen consumption in function of mole fraction of ethylene for thin EPR films (25 μm thick) exposed at 390 and 1050 Gy h^{-1} at 45 °C under 8.6×10^{4} Pa of pure oxygen. Comparison of predicted values (lines) with experimental ones (points) reported by Decker et al. (1973).

yields for alkyl radicals ranging from 2.7 to 3.7 in PE (Johnson et al., 1973; Dole and Patel, 1977; Gvozdic and Dole, 1980), and 2.4 to 2.6 in PP (Dole, 1973). However, the sensitivity of this method, to detect the totality of the alkyl radicals formed during irradiation, is questionable.

Values of the different kinetic parameters are presented in Table 4. These values seem to be quite realistic. As an example, termination rate constants respect well the theoretical hierarchies established for radicals reactivities (Howard and Ingold, 1967):

Alkyl radical $\gg$ peroxyl radical $= > k_4 > k_5 > k_{60}$

Secondary peroxyl radical $\gg$ tertiary peroxyl radical $= > k_{60S} > k_{60TS} > k_{60T}$

The kinetic model can be now used to predict some important quantities, closely linked to the polymer fracture behaviour, such as the radiation-chemical yield for chain scission and the ratio between the radiation-chemical yields for crosslinking and chain scission (see Table 5). The relatively poor PP stability to radiooxidation (against PE one) is well put in evidence.

But, the kinetic model can be also used to predict the radiation-chemical yields for EPR radiooxidation. As an example, the radiation-chemical yields for oxygen consumption and hydroperoxide build-up have been calculated for a series of three EPR differing essentially by their mole fraction of ethylene (37%, 73% and 86%) and their crystallinity degree (respectively 0%, 5% and 26%) at 390 and 1050 Gy h^{-1} at 45 °C under 8.6×10^{4} Pa of pure oxygen. They are compared to experimental ones reported in the literature in Figs. 1 and 2. In both cases, it is found a satisfying agreement between the theory and experiments.

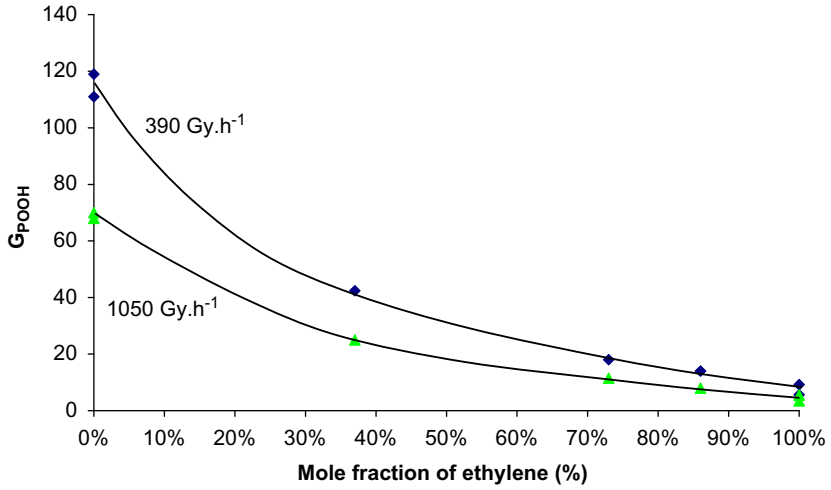

Fig. 2. Radiation-chemical yield for hydroperoxide build-up in function of mole fraction of ethylene for thin EPR films (25 μm thick) exposed at 390 and 1050 Gy h^{-1} at 45 °C under 8.6×10^4 Pa of pure oxygen. Comparison of predicted values (lines) with experimental ones (points) reported by Decker et al. (1973).

4. Conclusion

Despite the complexity of the mechanism and the corresponding kinetic model, it has been demonstrated that it is now possible to take into account several reactive sites in kinetic modelling. A satisfying agreement has been obtained between the model predictions and the experimental results for ldPE, hdPE, IPP, APP and EPR radiooxidation, which has allowed to determine the rate constants of the different elementary reactions. However, the validity of the kinetic model will be considered totally checked if this latter also satisfyingly predicts experimental results for thermal oxidation. Results are in progress at the laboratory and will be presented in a future communication.

References

Audouin, L., Gueguen, V., Tcharkhtchi, A., Verdu, J., 1995. 'Close loop' mechanistic schemes for hydrocarbon polymer oxidation. Journal of Polymer Science, Part A: Polymer Chemistry 33, 921.

Carlsson, D.J., 1993. Degradation and stabilisation of polymers subjected to high energy radiation. In: Scott, G. (Ed.), Atmospheric Oxidation and Antioxidants, Vol. II. Elsevier, Amsterdam, pp. 495.

Charlesby, A., 1960. Atomic Radiation and Polymers. Pergamon Press, London.

Chapiro, A., 1962. Radiation Chemistry of Polymeric Systems. Interscience Publishers Inc., New-York.

Colin, X., Audouin, L., Verdu, J., 2004. Determination of thermal oxidation rate constants by an inverse method. Application to polyethylene. Polymer Degradation and Stability 86, 309.

Colin, X., Monchy-Leroy, C., Audouin, L., Verdu, J., 2007. Lifetime prediction of polyethylene in nuclear plants. Nuclear Instruments & Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 265 (1), 251.

Decker, C., Mayo, F.R., Richardson, H., 1973. Aging and degradation of polyolefins. III. Polyethylene and ethylene–propylene copolymers. Journal of Polymer Science: Polymer Chemistry Edition 11, 2879.

Denisov, E.T., Afanas'ev, I.B., 2005. Oxidation and Antioxidants in Organic Chemistry and Biology. Taylor and Francis, CRC Press, Boca Raton.

Dole, M., 1973. The Radiation Chemistry of Macromolecules, vol. II. Academic Press, New York.

Dole, M., Patel, V.M., 1977. Comparison of irradiation crosslinking and chain scission in extended chain and bulk film samples of liner polyethylene. Radiation Physics & Chemistry 9, 433.

Emanuel, N.M., Buchachenko, A.L., 1987. Chemical Physics of Polymer Degradation and Stabilization (New Concepts in Polymer Science). VNU Science press, Utrecht.

Fayolle, B., Richaud, E., Colin, X., Verdu, J., 2008. Review: degradation induced embrittlement in semi-crystalline polymers having their amorphous phase in rubbery state. Journal of Materials Science 43, 6999.

Gvozdic, N., Dole, M., 1980. Alkyl free radical yields in the γ-ray irradiation of polyethylene at 77 K. Radiation Physics & Chemistry 15, 435.

Hairer, E., Wanner, G., 1991. Solving Ordinary Differential Equations II—Stiff and Differential–Algebraic Problems. Springer, Berlin.

Howard, J.A., Ingold, K.U., 1967. Absolute rate constants for hydrocarbon autoxidation. VI. Alkyl aromatic and olefinic hydrocarbons. Canadian Journal of Chemistry 45, 793.

Johnson, D.R., Wen, W.Y., Dole, M., 1973. Radiation chemistry of polyethylene. XII. Alkyl radical decay and amorphous content. The Journal of Physical Chemistry 77, 2174.

Kamiya, Y., Niki, E., 1978. Oxidative degradation. In: Jellinek, H.H.G. (Ed.), Aspects of Degradation and Stabilization of Polymers. Elsevier Scientific Publishing Company, Amsterdam, pp. 86 (Chapter 3).

Khelidj, N., Colin, X., Audouin, L., Verdu, J., Monchy-Leroy, C., Prunier, V., 2006a. Oxidation of polyethylene under irradiation at low temperature and low dose rate. Part I—the case of "pure" radiochemical initiation. Polymer Degradation and Stability 91 (7), 1593.

Khelidj, N., Colin, X., Audouin, L., Verdu, J., Monchy-Leroy, C., Prunier, V., 2006b. Oxidation of polyethylene under irradiation at low temperature and low dose rate. Part II—low temperature thermal oxidation. Polymer Degradation and Stability 91 (7), 1598.

Korcek, S., Chenier, J.H.B., Howard, J.A., Ingold, K.U., 1972. Absolute rate constants for hydrocarbon autoxidation. XXI. Activation energies for propagation and the correlation of propagation rate constants with carbon–hydrogen bond strengths. Canadian Journal of Chemistry 50, 2285.

Mita, I., 1978. Effect of structure on degradation and stability of polymers. In: Jellinek, H.H.G. (Ed.), Aspects of Degradation and Stabilization of Polymers. Elsevier Scientific Publishing Company, Amsterdam, pp. 260–262 (Chapter 6).